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Nanodiamonds

Evidence of Diamond Nanowires Formed inside Carbon Nanotubes from Diamantane Dicarboxylic Acid**

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Three-dimensional (3D) sp^2 and sp^3 crystalline carbon structures have a variety of applications.[1] With the advent of nanotechnology,[2] zero-dimensional (0D, fullerenes),[3] one-dimensional (1D, carbon nanotubes, CNTs),[4] two-dimensional (2D, graphene)[5] sp^2 crystalline carbon, and a variety of 3D sp^3 (nanodiamond) nanostructures were discovered successively. Adamantane, the simplest 0D sp^3 diamondoid, has long been known. Higher diamondoids were first isolated from petroleum only about a decade ago.[6] The growth of diamond from such nanodiamonds[7] was only just recently achieved.[8] The synthesis of diamond wires with diameters of 50–100 nm has been achieved,[9] but the preparation of diamond nanowires with sub-nanometer diameter has not been achieved so far.

Diamondoids have been found to have strong affinity towards compatible host structures, such as cyclodextrins[10] and CNTs.[11] Analogous to the fabrication of 1D sp^2 CNTs from 0D sp^2 fullerenes,[12,13] we propose that diamondoids may also fuse and transform into 1D sp^3 diamond nanowires. Templated growth of these nanowires from 1D diamondoid assemblies confined in CNTs provides a probable pathway through a "face-fused" reaction. However, the fusion reaction of adamantane into diamond nanowires has been shown to be energetically unfavorable.[11]

Herein, we present theoretical and experimental evidence for the feasibility of a fusion reaction of diamondoid derivatives containing relatively reactive functional groups, diamantane-4,9-dicarboxylic acid (**1**),[14] to 1D diamond nanowires inside CNTs. The bisapical diamondoid diacid is more reactive than the pristine diamondoid, requiring milder reaction conditions. Unlike in 3D space, the diamantane dicarboxylic acid molecules are pulled inside a CNT by an effective "capillary force" that originates in the stabilization of the molecule inside the surrounding nanotube. This capillary force, in turn, compresses the enclosed molecular array of **1** axially and aligns the molecules favorably. In this special surrounding environment, **1** may react in an unusual way to create an extended diamondoid cage during a mechanistically complex polymerization process. Hence, the fusion of **1** under the confinement of CNTs may be a promising choice to yield diamond nanowires.

Compound **1** was sublimed and self-assembled into the quasi 1D space of double-wall CNTs (DWCNTs) by a vapor phase reaction.[11,13,16] The sublimation temperature of **1** was measured by thermogravimetry (TG) to start at 300 °C under air atmosphere (Supporting Information, Figure S1). An encapsulation temperature of 280 °C was chosen for **1** at 10^{-6} Torr owing to its relatively low sublimation temperature in vacuo.

Similar to adamantane,[11,17] the encapsulation of **1** is highly selective with respect to the CNT inner diameter (D_{inner}). We observed no encapsulated **1** in DWCNTs which have $D_{\mathrm{inner}} < 0.8$ nm (Figure 1 a). However, we found **1** well aligned along the axis of DWCNTs with compatible $D_{\mathrm{inner}} \approx 1.0$ nm (Figure 1 b), consistent with computational results for diamondoid encapsulation.[17] Multiple arrays of encapsulated molecules can often be found in CNTs with much wider D_{inner} (Figure 1 c). The observed high-resolution transmission electron microscopy (HR-TEM) images are consistent with the corresponding simulated TEM images (Figure 1, insets).

Our main purpose is to explore the synthesis feasibility of diamond nanowire, which is a promising tip for scanning-probe microscopy,[25] from 1D assemblies of **1** in CNTs. As demonstrated in the diamond formation by chemical vapor deposition (CVD)[15] and thermal annealing of adamantane inside CNTs,[11] hydrogen plays a crucial role in retaining the sp^3 diamond cages. The as-produced diamondoid 1D assemblies in DWCNTs (**1**@DWCNTs) were annealed at 600 °C for 12 h under a flow of hydrogen. Carbon-based nanowires (CNWs) are then found inside DWCNTs with $D_{\mathrm{inner}} \approx 1.3$ nm (Figure 2). The rod-shaped product has a diameter about 0.78 nm from the HR-TEM image (dark contrast in Figure 2 a). The CNW is very stiff and straight, and robust under

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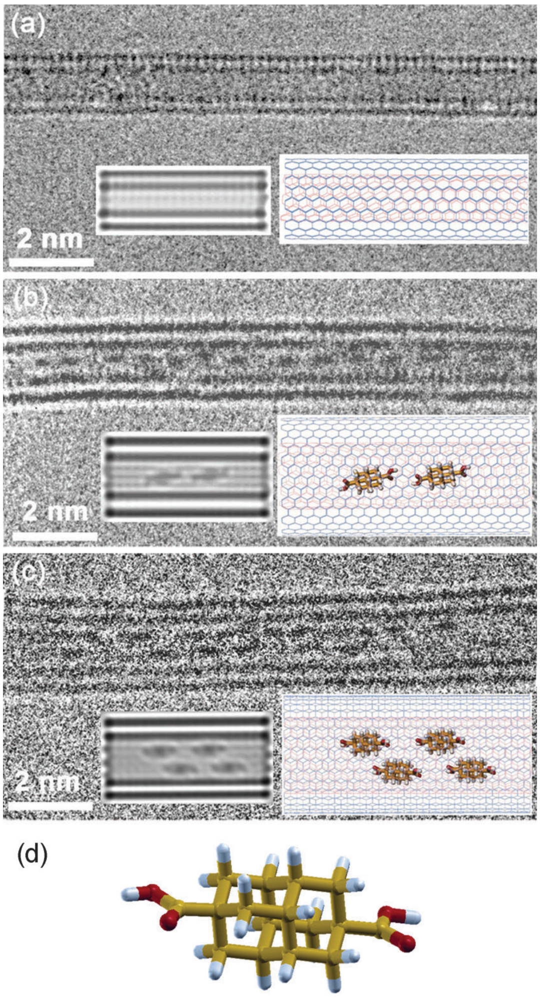

Figure 1. HR-TEM and simulated images, as well as model structures of a) empty DWCNTs ($D_{\text{inner}} < 0.8$ nm), b) linear diamondoid arrays inside DWCNTs ($D_{\text{inner}} \approx 1$ nm), c) multiple diamondoid arrays inside DWCNTs ($D_{\text{inner}} \approx 1.3$ nm), and d) optimized structure of the diamantane-4,9-dicarboxylic acid molecule **1**; C yellow, O red, H white.

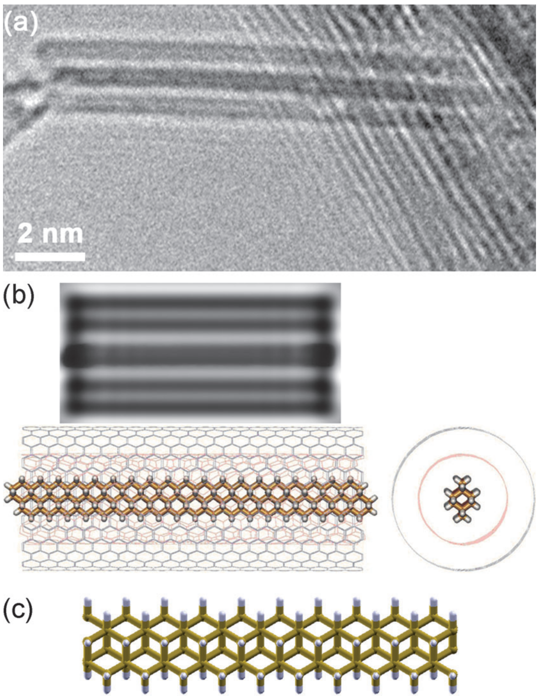

Figure 2. a) HR-TEM image of a carbon-based nanowire inside a DWCNT; b) simulated image of a diamond nanowire inside a DWCNT along with the corresponding structural model; c) structural model of a diamond nanowire.

electron beam irradiation (1.1×10^5 [e]/(nm^{2}s)) even though it was broken during sample preparation (Figure S2). No rod structures have been observed in DWCNTs with a smaller D_{inner} of around 1.0 nm.

Anhydride polymers are generally expected to form during thermal annealing of 1D assemblies of **1** under hydrogen atmosphere, since anhydrides can be produced by dehydration of carboxylic acids.[26] However, the simulated HR-TEM image of anhydride polymer in a DWCNT (Figure S3) is different to our observed structure (Figure 2a). Diamantane linear polymer chains may also be obtained if anhydride polymers are further annealed under a hydrogen atmosphere through the decarboxylation of anhydrides.[27] However, the simulated HR-TEM images of diamantane polymers inside DWCNTs (Figure S4) also differ from the observed structure (Figure 2a). Among the simulated TEM images of different structures considered, we found that a diamond nanowire with the (110) crystal face inside a DWCNT, shown in Figure 2b and c, is consistent with our observed HR-TEM images. Other crystal directions of the nanowire yield slightly different simulated TEM images. For the sake of completeness, we show the simulated TEM image of the diamond nanowire with the (100) crystal face in Figure S5. Comparing the simulated TEM images of the different candidate structures, we conclude that Figure 2a most likely represents a nanowire with the (110) face. Its simulated image in Figure 2b shows the rod border darker than the center of the rod, which is different to the nanowire with the (100) face in Figure S5.

Our TEM observation supports our conjecture that CNT can provide an extraordinary environment for chemical reactions which are almost impossible in conventional chemistry. Diamond nanowires may be produced from fusion reaction of **1** inside CNTs under hydrogen atmosphere [Eq. (1)]

$$C_{14}H_{18}(COOH)_2(g) + 2\,H_2(g) \rightarrow 2\,C_8H_8(s) + 4\,H_2O(g) + 56.2\ \text{kcal}\,\text{mol}^{-1} \tag{1}$$

where “C_8H_8” is the repeating unit of an infinite diamond nanowire.

Unlike for the formation of a diamantane linear polymer chain as the final product, our ab initio density functional theory (DFT) calculations indicate that the formation of a diamond nanowire from **1** in hydrogen atmosphere is an exothermic process with $\Delta E = +56.2\ \text{kcal}\,\text{mol}^{-1}$. We found that the capillary force that pulls a diamantane dicarboxylic acid molecule inside an (8,8) nanotube amounts to 0.4 nN.

This translates to a formidable equivalent pressure of over 400 MPa, which should compress the molecules axially and favor their fusion. To study the feasibility of the reaction in Equation (1), we investigated the dynamics of an infinite array of **1** in the presence of hydrogen inside a cylindrical cavity representing the enclosing (8,8) nanotube using DFT-based molecular dynamics simulations and total free energy calculations. The axial intermolecular distance was reduced to mimic the capillary pressure, and the system was coupled to a thermostat at 1500 K.

The results of our MD simulation, presented in the Supporting Information, reveal several energetically attractive pathways and help identify intermediate steps (shown in Figure S6) leading to the formation of the diamond nanowire. We find that at high temperatures, detachment of CO_2 from the acid molecules competes with the detachment of hydrogen atoms from carbon atoms, thus opening the way to interconnecting neighboring molecules by covalent C–C bonds. Before forming H_2 molecules, hydrogen atoms may attach to the terminating COOH groups. Our simulations indicate the possibility of further hydrogenation of these groups, which leads to the formation of H_2O molecules. Additional hydrogenation of the carbon-based backbone structure following H_2O desorption completes the attachment of one C_8H_8 unit to the diamond nanowire.

The encapsulation and annealing processes were also characterized by Raman scattering and attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR). A new Raman feature at 1245 cm^{-1} was detected in the annealed sample (Figure 3 a). After encapsulation, the C–H wagging modes around 1100–1300 cm^{-1} of diamondoids[18] and their strong C–H stretching modes around 2800–3000 cm^{-1} are totally suppressed in the Raman spectra because of the surrounding CNT walls (Figure S7). DWCNTs containing diamondoids can hardly be distinguished from pristine DWCNTs in Raman spectra (Figure S8), but can easily be distinguished in the ATR-FTIR spectra as show in Figure 3 b.

The new Raman feature at 1245 cm^{-1} does not originate from C–H vibrations of DWCNTs exposed to hydrogen, since it was not detected in samples of empty DWCNTs (Figure 3 a, yellow) and adamantane encapsulated DWCNTs under similar hydrogen treatments (Figure S9).[11] This Raman peak is, therefore, caused by fusion products of **1**, which might come from the C–C stretch of the diamond nanowires inside DWCNTs. The C–C stretching mode of **1** was detected at 712 cm^{-1} in the solid sample (Figure S8), whereas that of 1D rod-shaped diamondoids was reported to be at 680 cm^{-1} with weak companion peaks (ca. 50 cm^{-1}).[18] Furthermore, bulk crystalline diamond has a characteristic sharp Raman feature at 1332.5 cm^{-1}.[19] In small diamond fragments, this Raman peak has been found to shift from 1332.8 to 1329.6 cm^{-1} and become broader on decreasing the particle size from 120 to 28 nm.[20] In general, the frequency of the C–C stretching mode of narrow diamond nanowires can change from 700 cm^{-1} to 1332 cm^{-1} depending on their diameter. The presence of the 1245 cm^{-1} Raman feature in the as-produced sample, which should also reflect the interaction of the converted diamondoid with the surrounding CNT walls, provides further support for the formation of narrow diamond nanowires.

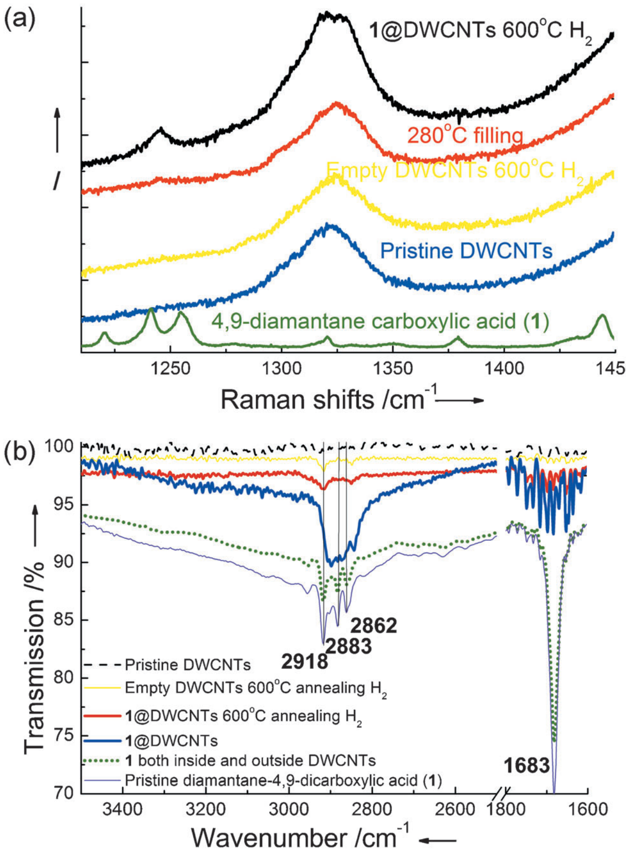

Figure 3. Effect of annealing at 600 °C in an H_2 atmosphere on a) Raman and b) ATR-FTIR spectra of **1** encapsulated inside DWCNTs.

In ATR-FTIR spectra of solid **1** (Figure 3 b, thin purple line), we observed one strong band associated with the dicarboxylic carbonyl group (C=O) stretching at 1683 cm^{-1}, three medium-strong bands at 2918 cm^{-1} (anti-symmetric CH_2 stretch), 2883 cm^{-1} (CH stretching vibration coupled with symmetric CH_2 stretching), and 2862 cm^{-1} (CH stretching),[28] and one broad band of dicarboxylic O–H stretching at 2500–3500 cm^{-1}. The overall ATR-FTIR features of **1** condensed both inside and outside of DWCNTs after encapsulation (Figure 3 b, dotted green line) are virtually the same as in the pristine sample (Figure 3 b). There was no decomposition observed during the encapsulation of **1** at 280 °C, which can also be confirmed by the Raman spectra (Figure S10). Three absorption bands of C–H stretching modes are broadened and overlap with each other in the **1**@DWCNT sample as a result of the interaction with the encapsulating tube, whereas the C=O and O–H stretching modes of the carbonyl group are hardly detectable (Figure 3 b). After annealing at 600 °C under a hydrogen atmosphere the O–H stretching at 2500–3500 cm^{-1} disappear and the C=O stretching at 1683 cm^{-1} becomes broad, and weakens further (Figure 3 b, red). Only very weak C–H stretching bands were observed, broader but comparable to those of the empty DWCNTs under similar treatment, suggesting the presence of a fusion reaction during annealing. It is hard to further analyze these C–H bands owing to their low intensities.

The as-produced CNWs are stable inside DWCNTs under electron-beam irradiation with a current density below 1.1×10^5 [e]/(nm^2 s). Under irradiation at higher current densities of 1.7×10^5 [e]/(nm^2 s) for less than 10 s, however, carbon nanostructures enclosed inside DWCNTs, both before and after annealing, underwent a structural transformation to onion-like sp^2 structures. Figure S11a shows a HR-TEM image of the transformed structure after an electron energy loss spectroscopy (EELS) measurement. The ratio of electron transition from the 1 s level to the π^* band and σ^* band, $[\pi^*/(\pi^*+\sigma^*)]$, was estimated to be 0.17 according the carbon K-edge of the as-produced structure (Figure S11b).[21] The ratio of sp^2 carbon is calculated to be 68 %.[22,23] Under strong electron-beam irradiation, even pristine DWCNTs are damaged (Figure S12a). However, no onion structures were formed since no carbon nanostructures were present inside CNTs. The $\pi^*/(\pi^*+\sigma^*)$ ratio was estimated to be 0.14 and the sp^2 carbon concentration to be 56 % in the empty DWCNTs case (Figure S12b), consistent with the reported EELS measurement of CNTs.[23] The sp^2 ratio of the observed onion-like structure is higher than the empty DWCNT, indicating increased sp^2 hybridization. Such a transformation is consistent with a 1D carbon phase calculation, in which CNTs represent the energetically most preferred form at diameters smaller than 2.7 nm.[24] Under high-intensity electron-beam irradiation, the encapsulated diamond nanostructures were dehydrogenated and reconstructed into sp^2 structures. Termination by heavier elements than hydrogen may suppress this transformation.[29]

The HR-TEM images, Raman spectra, and observed structural transformations suggest that the CNWs are diamond nanowires, as expected from the reaction scheme and DFT calculations. However, the full characterization of the CNWs has not been realized yet. In addition to the structural transformation under intense electron-beam irradiation, the small proportion of DWCNTs with D_{inner} around 1.3 nm, along with the low encapsulation yield at these diameters, make the characterization even more difficult. Improving the encapsulation yield of **1** in CNTs with $D_{\text{inner}}\approx 1.3$ nm is crucial to fully characterize the nature of the CNWs. We found that capping both ends of the CNTs by C_{60} fullerenes can significantly improve the encapsulation yield of **1** in CNTs with large diameters. However, the presence of the capping fullerenes impedes hydrogen circulation during annealing. Functional higher diamondoid derivatives with relative larger dimensions, which can be compatibly encapsulated into DWCNTs with $D_{\text{inner}}\approx 1.3$ nm, could be promising candidates to produce diamond nanowires in DWCNTs.

In summary, CNWs with diameters about 0.78 nm have been produced by thermal annealing of **1** under the confinement of DWCNTs in hydrogen atmosphere. ATR-FTIR spectra reflect significant changes during the encapsulation and annealing procedure. The as-produced samples gave a new Raman feature at 1245 cm^{-1} and underwent a structural transformation into sp^2 nanostructures under intense electron-beam irradiation. Our experimental and theoretical data suggest that the CNWs are diamond nanowires produced from fusion reaction of **1** under the extraordinary conditions provided by the encapsulating CNTs.

Experimental Section

DWCNTs (Toray Co., 2 mg) were heated at 480 °C for 30 min in air to open the caps. The open-ended DWCNTs were degassed at 300 °C for 2 h and then sealed in the presence of **1** (100 mg) under a vacuum of 10^{-6} Torr. Following sublimation of **1**, individual molecules were pulled inside the DWCNTs by a force resembling the capillary force. The as-produced sample was washed by acetone and dried in the oven at 90 °C overnight. Samples obtained in this way were subsequently annealed at 600 °C for 12 h while being flushed by pure hydrogen with a flow rate of 200 sccm. HR-TEM measurements of **1**@DWCNTs and CNW@DWCNTs were performed by a JEOL JEM-ARM200F microscope with a CEOS probe and image aberration correctors and a JEOL JEM 2100F microscope, respectively, operated at 80 KV at room temperature.

Total energy calculations and canonical molecular dynamics simulations of infinite periodic arrays of molecules in the enclosing potential[11] of a CNT were performed using ab initio density functional theory (DFT-LDA) computations as implemented in the SIESTA code.[30] We used a double-ς polarized basis and sampled the 1D Brillouin zone of the molecular array inside the nanotube by 16 k-points. The self-consistent charge density was determined using a mesh cutoff energy of 100 Ry. Equilibrium geometries and vibration frequencies are presented for optimum structures, where none of the residual Hellmann-Feynman forces exceeds 10^{-2} eV Å^{-1}.

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